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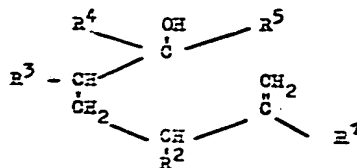
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(54) PRODUCTION OF ALK-1-EN-6-OLS AND NOVEL COMPOUNDS OF THIS TYPE

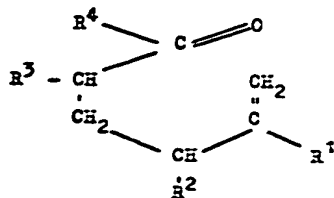
(71) We, BADISCHE ANILIN- & SODA - FABRIK AKTIENGESELLSCHAFT, a German joint stock company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
The present invention provides novel alk-1-en-6-ols of formula I:



(I)

in which R¹ denotes methyl, R² and R³ denote hydrogen, methyl or ethyl, R⁴ denotes methyl or ethyl and R⁵ denotes hydrogen or alkyl of from 1 to 6 carbon atoms.

We have found that these compounds and analogous compounds in which R¹ denotes ethyl may be produced from corresponding alk-1-en-6-ones of formula II:



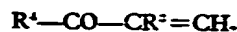
(II)

either by reaction (when R³ denotes alkyl) with an organometallic compound of the formula M—R³, in which M denotes an alkali metal, in particular lithium, or the magnesium

[Price 25p]

halo residue of a Grignard compound and R⁵ denotes alkyl of 1 to 6 carbon atoms or, (when R⁵ denotes hydrogen) by reducing the carbonyl group to a hydroxyl group.

The starting compounds of formula II are known or are obtainable by known methods, for example by reacting alkenyl ketones of the formula



with olefins of the formula



Examples of these starting compounds are as follows:

- 1, 3- or 5- methylhept - 1 - en - 6 - one,
2-, 3- or 5- methyloct - 1 - en - 6 - one,
2-, 3- or 5- ethylhept - 1 - en - 6 - one,
2-, 3- or 5- ethyloct - 1 - en - 6 - one,
2,3-, 2,5- or 3,5- dimethylhept - 1 - en - 6 - one,
2 - methyl - 3 - ethylhept - 1 - en - 6 - one,
2 - methyl - 5 - ethylhept - 1 - en - 6 - one, or
2,3,5- trimethylhept - 1 - en - 6 - one.

Preferred starting compounds of formula II are those in which R¹ and R⁴ denote methyl and R³ denotes hydrogen, such as 2 - methyl - hept - 1 - en - 6 - one and 2,3 - dimethylhept - 1 - en - 6 - one.

By the organometallic compounds of formula M—R³ we particularly mean Grignard compounds of the type R³—MgCl and R³—MgBr, of which the chlorides are preferred for economic reasons. In the Grignard compounds the radical R³, which may contain up to 6 carbon atoms, may be, for example, methyl, ethyl, isopropyl, n-propyl, isobutyl, t-butyl, n-pentyl or n-hexyl. In view of the properties of the products of formula I obtained therefrom, methyl and ethyl magnesium chlorides are particularly important. The reaction of the organometal-

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lic compound of formula $M-R^3$ with the starting compound of formula I may be carried out according to generally known methods (see Kharash and Reinmuth: "Grignard Reactions of Non-metallic Substances", New York, Pentice-Hall Inc. 1954, pp. 138 ff and G. E. Coates: "Organometallic Compounds", London, Methusen & Co. Ltd., pp. 1-87).

For example, the ketone of formula II may be added dropwise to a solution of the organometallic compound in an inert solvent such as tetrahydrofuran or ether, at temperatures ranging from 0° to 50°C, preferably from 10° to 30°C, and the reaction mixture allowed to continue reacting for a further 30 minutes to 5 hours with stirring. Advantageously, from 1.05 to 1.3 moles of organometallic compound is used per mole of ketone.

In general, the operation is carried out in about 1 to 3 molar solutions. The reaction mixture is then mixed with about 100 ml of water per mole of metal or with at least 1 mole of sulfuric acid in dilute form, and the separating organic layer is removed and fractionally distilled under reduced pressure. Where alkali metal alkyls are used, such as lithium methyl, it is preferred to use ether as solvent.

The reduction of ketones of formula II to the corresponding alcohols may also be carried out by usual methods such as by reducing with complex hydrides such as lithium borohydride, lithium aluminium hydride and sodium borohydride. By way of example, the reaction with sodium borohydride is described in detail below.

The ketone is dissolved in a lower alcohol (having up to 4 carbon atoms) and sodium borohydride is added portionwise to this solution at temperatures ranging from 10° to 50° C, the reaction mixture then being stirred for about 5 hours at the reaction temperature. The alcohol is then distilled under reduced pressure and the residue is mixed with water. This mixture is then extracted several times with a water-immiscible organic solvent such as diethyl ether and the organic solution thus obtained is dried and then fractionally distilled at subatmospheric pressure. Preferably from 200 to 400 ml of alcohol, one third of a mole of sodium borohydride and 100 ml of water are used per mole of ketone.

The alk -1- en - 6 - ols of the invention are noteworthy for their novel and characteristic scents and, by reason of this property, they have a wide variety of applications in perfumery and cosmetics and in improving the odours of industrial products such as detergents, glues and polymer dispersions. The substance of formula I generally have a linalool type of odour but are more resistant to acids and alkalis than

linalool, so that they are particularly suitable for perfuming soaps, detergents, etc. The invention therefore includes odoriferous compositions containing an alk - 1 - en - 6 - ol according to the invention as odour-imparting ingredients.

The following Examples illustrate the invention.

EXAMPLE 1

2,6 - Dimethylhept - 1 - en - 6 - ol

A solution is prepared in a conventional manner from 89.5 g (1.2 moles) of methyl magnesium chloride and 300 ml of tetrahydrofuran, and 126 g (1 mole) of 2 - methylhept - 1 - en - 6 - one are gradually added at 20°C. The reaction mixture is then worked up to provide 2,6 - dimethylhept - 1 - en - 6 - ol by conventional techniques. The yield of pure product is 91%; b.p. 40-45°C/0.7 mm; n_D^{25} 1.4427.

The compound smells of bergamot with a minty note.

EXAMPLE 2 to 4

Following the general procedure described in Example 1 the following compounds are obtained:

(2) 2,3,6 - trimethylhept - 1 - en - 6 - ol, b.p. 87-89°C/19 mm Hg, n_D^{25} 1.4456, from 2,3 - dimethylhept - 1 - en - 6 - one and methyl magnesium chloride; yield 90%; odour: similar to linalool but with a campharous note;

(3) 2,6 - dimethyloct - 1 - en - 6 - ol, b.p. 86°C/11 mm Hg, n_D^{25} 1.4473; from 2 - methylhept - 1 - en - 6 - one and ethyl magnesium bromide; yield 75%; odour: similar to lilac;

(4) 2,6,7 - trimethyloct - 1 - en - 6 - ol, b.p. 97-98°C/12 mm Hg, n_D^{25} 1.4502, from 2 - methylhept - 1 - en - 6 - one isopropyl magnesium bromide, yield 55%; odour: fruity, reminiscent of peach/apricot.

EXAMPLE 5

2 - Methylhept - 1 - en - 6 - ol

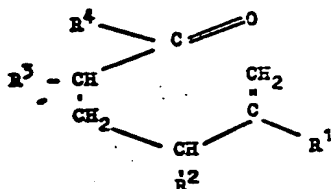
10 g of sodium borohydride are added portionwise to a solution of 126 g of 2 - methylhept - 1 - en - 6 - one and 250 ml of ethanol at room temperature, and the mixture is allowed to react for a further five hours, whereupon it is worked up in the usual manner to give the desired product. The yield is 76%, b.p. 89-91°C/22 mm Hg, n_D^{25} 1.4422.

Odour: similar to linalool with a fresh note.

If the sodium borohydride is replaced by an equal weight of lithium borohydride or lithium aluminium hydride, substantially the same yield is obtained.

WHAT WE CLAIM IS:—

1. Alk - 1 - en - 6 - ols of the formula



(I)

5 in which R¹ denotes methyl, R² and R³ denote hydrogen, methyl or ethyl, R⁴ denotes methyl or ethyl and R⁵ denotes hydrogen or alkyl of from 1 to 6 carbon atoms.

2. 2,6 - Dimethylhept - 1 - en - 6 - ol.

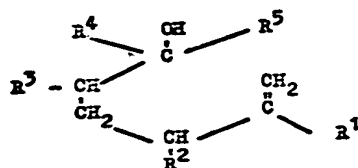
3. 2,3,6 - Trimethylhept - 1 - en - 6 - ol.

10 4. 2,6 - Dimethyloct - 1 - en - 6 - ol.

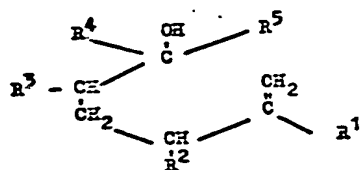
5. 2,6,7 - Trimethyloct - 1 - en - 6 - ol.

6. 2 - Methylhept - 1 - en - 6 - ol.

7. A process for the manufacture of an alk - 1 - en - 6 - ol of the formula



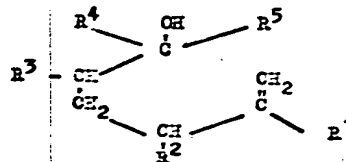
15 in which R¹ and R⁴ denote methyl or ethyl, R² and R³ denote hydrogen, methyl or ethyl and R⁵ denotes alkyl of from 1 to 6 carbon atoms, comprising reacting an alk - 1 - en - 6 - one of the formula:



(II)

in which R¹, R², R³ and R⁴ have the meanings given above, with an organometallic compounds of the formula M—R⁵, in which M denotes alkali metal or the magnesium halo residue of a Grignard compound and R⁵ has the meanings given above.

8. A process for the manufacture of an alk - 1 - en - 6 - ol of the formula



in which R¹, R², R³ and R⁴ have the meaning given in claim 7 and R⁵ denotes hydrogen, comprising subjecting a corresponding alk - 1 - en - 6 - one to reduction to reduce the carbonyl group to a hydroxyl group.

9. A process as claimed in claim 7 wherein an alk - 1 - en - 6 - one of formula (II) is reacted with methyl magnesium chloride or ethyl magnesium chloride.

10. A process as claimed in claim 8 wherein an alk - 1 - en - 6 - one is reacted with lithium borohydride, lithium aluminium hydride or sodium borohydride.

11. A process for the manufacture of an alk - 1 - en - 6 - ol substantially as hereinbefore described and exemplified.

12. Alk - 1 - en - 6 - ols when manufactured by a process as claimed in any of claims 7 to 11.

13. Odoriferous compositions containing an alk - 1 - en - 6 - ol as claimed in any of claims 1 to 6 and 12 as odour-imparting ingredient.

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